PB-237 828-T

SULFUR POLLUTION

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September 1974

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U. S. DEPARTMENT OF COMMERCE

212040

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PB 237 828-T

EPA-TR 52-75

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In La Recherche 3(27), Oct. 1972, pp. 884-886.

"In Sweden, experts have calculated that it will be necessary to spend $200 million per year to reduce sulfur pollution by 90%."

As a number of reports have recently demonstrated, sulfur pollution is beginning to reach critical levels in some parts of the world. Sulfur dioxide (SO_2) and sulfuric acid (H_2SO_4), resulting, along with other gases, from the combustion of fossil fuels (carbon, petroleum, gas) are poisoning the air of cities, corroding metal coatings and paints, increasing the acidity of rivers and lakes, and decreasing the growth of vegetation. Today, man's contribution to the sulfur cycle is almost half the amount generated by natural processes. Of the total of 500 million tons of sulfur passing through the atmosphere, ground and water per year, the quantity from sources resulting from human activity (anthropogenic sources) is approximately 150 million tons. In the year 2000, the amount generated by human activity will be equal to that generated by nature, and it will probably be greater in the northern hemisphere. It is therefore impossible to consider the sulfur cycle

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Translated from the French for Technical Publications Branch, Information Services Division, EPA, by Leo Kanner Associates, P.O. Box 5187, Redwood City, CA 94063, (415) 365-3046, September 1974.

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in its natural ecosystem without taking into account the changes man has produced.

Study of this cycle is interesting for several reasons. The different forms of sulfur pollution are fairly well known. The effects of this substance on living organisms and different types of materials are also known. The modes of transport of sulfurous pollutants by air or water have been analyzed and their long-distance effects have been measured. Finally, the emission of sulfur products is very closely related to energy production, which of course, is constantly increasing throughout the world. Study of a global model of the emission and uses of sulfur in the ecosystem thus affords a means of measuring the degree to which man is affecting natural cycles, permitting conclusions on ways of protecting the environment. To one extent or another, this has been the task of ecologists throughout the world.

The element sulfur (S) is found in a number of stable chemical compounds where it may be in a positive or negative oxidation state. It may be reduced to hydrogenated sulfur or sulfurated hydrogen (H_2S) or oxidized to sulfur dioxide (SO_2), and then to sulfur trioxide (SO_3). The oxidation or reduction rates of sulfur compounds depend on a large number of factors, particularly the effect of UV radiation or the presence of catalytic particles (dust, aerosols) such as those found in the smog of large cities. Hydrogen sulfide (H_2S), resulting in large part from the degradation of organic materials by bacteria, may be oxidized to SO_2 by atomic oxygen (O), molecular oxygen (O_2) or ozone (O_3). After the absorption of energy in the form of ultraviolet radiation, the excided SO_2 reacts with the molecular oxygen to yield SO_3, and, in the presence of water, sulfurous acid H_2SO_3, which is quickly oxidized to sulfuric acid H_2SO_4. Most of the sulfur compounds pass into

the atmosphere from various sources such as combustion stacks, areas of decomposition of organic matter, the surface of the ocean and volcanoes. These compounds are carried through the atmosphere by winds and turbulence, and, after a given period of time, are deposited on the ground or in the ocean.

Sources of Sulfur Compounds

95% of the sulfur emissions resulting from human activity occur in the form of SO_2. The total quantity of anthropogenic emissions (resulting primarily from the activity of thermal power plants for production of electricity) has been estimated at 150 million tons SO_2 per year. 93.5% of this quantity comes from the northern hemisphere, and only 6.5% from the southern hemisphere.

Sulfur emissions from volcanoes represent only a fairly small proportion of the total sulfur compounds entering the atmosphere. The total quantity of gases (SO_2, SO_3, H_2S) and sulfates has been estimated at 2 million tons per year.

The ocean contains approximately 2.65 mg of "salts" in the form of sulfates (SO_4^{--}) per gram of water. Ten percent of this sulfate is carried to the continents by wind and clouds. The annual production of sulfates by the ocean is estimated to reach 120 million tons per year.

Anaerobic bacteria produce hydrogen sulfide (H_2S) during processes of organic decomposition. Swamps, areas of vegetable decomposition, and the decomposition of marine organisms and algae in coastal zones release a total annual quantity of H_2S which is estimated at 268 million tons.

The sulfur-containing substances present in the atmosphere may be "washed out" by rain to accumulate on the ground. SO_2 reaching the surface of the earth directly is captured by plants and the soil. Sulfur thus enters into the composition of organic substances essential to vegetation. Sulfates may

also be deposited dry on the earth's surface. It has been calculated that approximately 13 million tons of sulfate from the ocean are deposited on the continents. The total amount of SO_2 and sulfates "washed out" by rain in the atmosphere is approximately 258 million tons per year, while the fraction captured by plants or bacteria or deposited on the earth in dry form is 45 million tons for SO_2 and 30 million tons for sulfates.

The average time for H_2S, SO_2 and sulfates to remain in the atmosphere is shorter than one might initially expect. H_2S remains in the atmosphere for an average of seven days before being oxidized to SO_2, while the latter compound, due to the variety of processes by which it can be oxidized, remains for periods of between 12 hrs and six days. Finally, sulfates are recycled only after an average of one week. A large part of the sulfur compounds deposited on the earth are removed to the ocean via run-off and rivers. Up to the present it has been extremely difficult to estimate the total quantity carried to the ocean annually by rivers. This quantity includes sulfur derivatives from the erosion of rock (40 million tons), sulfur-containing fertilizers (30 million tons) and deposits resulting from atmospheric precipitation (approximately 160 million tons). These figures, based on 1960 estimates, are given here only as an indication, since they have not yet been checked and updated by experts. However, they do give some idea of the quantities involved.

Sweden and the Dangers of Sulfur Pollution

A report prepared by Swedish researchers and presented in Stockholm at the last international conference on the environment admirably demonstrated the long-term effects of sulfur pollution. This example, applied to Swedish territory, provides the initial elements for answers to the main questions on the transfer of pollutants through the atmosphere and on the effects of

SO_2 and sulfuric acid on population health, metal structures, vegetation and the fauna of rivers and lakes.

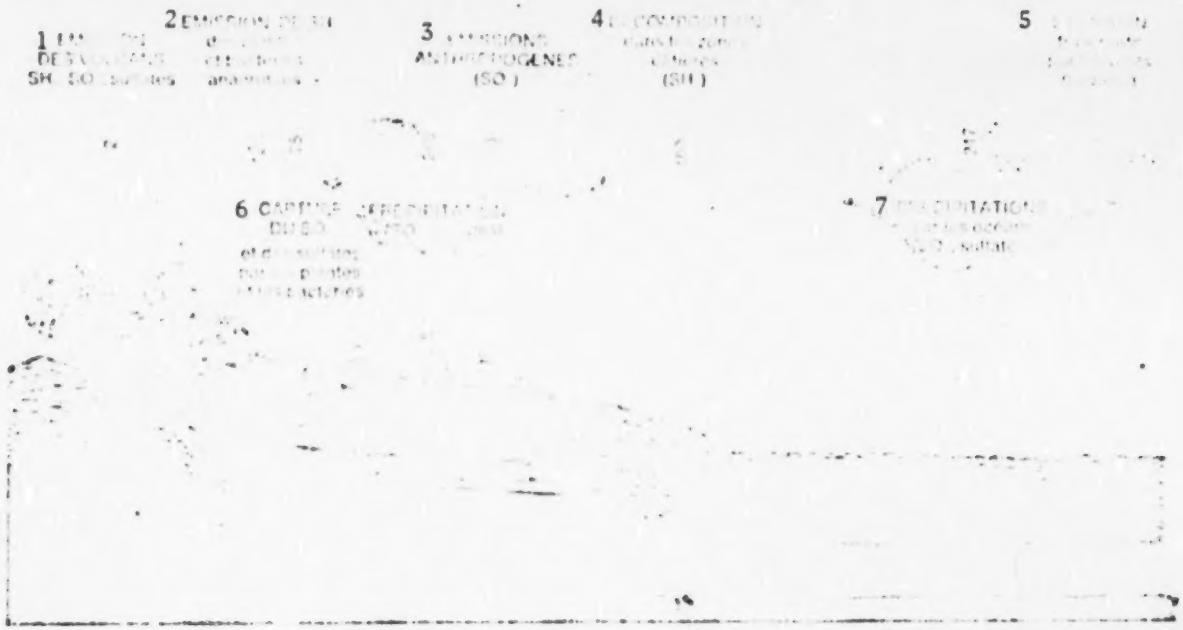

Fig. 1. [Caption illegible.]

Key:
1. Emissions from volcanoes: H_2S, SO_2, sulfates.
2. Emission of H_2S: plants and anaerobic bacteria.
3. Anthropogenic emissions (SO_2).
4. Decomposition in coastal areas (H_2S).
5. Marine salts carried by winds (sulfates).
6. Capture of SO_2 and sulfates by plants and bacteria.
7. Precipitation on the ocean (SO_2, sulfates).

First of all, the Swedish report clearly illustrates the fact that pollution by sulfur compounds extends well beyond national boundaries: it has been demonstrated that the pollutants may be deposited several thousand kilometers from their source. Thus 50% of the sulfur deposited on Swedish soil per year largely comes from central Europe and Great Britain.

Sweden alone emits approximately 1 million tons SO_2 per year, half of this from industry and the other half from domestic chimneys. The total

sulfur deposit per hectare per year reaches 9 kg in the southern part of the country and 5.7 kg in the north. The rate of corrosion in Stockholm is six times higher than in the surrounding countryside. Vegetation may undergo chronic damage from SO_2 concentrations as low as 0.05 ppm. The reduction in the growth rate of Swedish forests between 1950 and 1965 has been estimated at 0.3%. The authors of the report, however, estimate that before the end of this century the forest industry in southern Sweden will experience a decrease in raw material of 10% to 15% from current levels. The most spectacular effect of the depositing of sulfur products on the earth's surface is probably the increase in the acidity of lakes. In most Swedish lakes the pH has decreased 8% to 23% over the last ten years. In 50 years some lakes will have reached a pH of 5, below which fish will be unable to survive.

The impact of sulfur pollution on the health of the population is obviously much more difficult to measure, and considerable research is still necessary before the degree of increase in respiratory diseases, for example, as a function of the increase in SO_2 concentration can be definitely established. It is easier, however, to estimate the cost represented by the retardation of vegetation growth: if the speed of deposit of sulfur products continues to increase at the current rate, the effect on the 100,000 km^2 of Swedish forest will be a 10% to 15% decrease in vegetation, or a cost of $35 million for the year 2000. The report estimates that for [line(s) missing in original], the overall cost computed on the basis of current production and known reduction methods will increase to $20 million per year. And for a 90% reduction, this will be $200 million per year.

Basic Steps in Prevention: Simulation and Observation of Industrial Pollution

The question remains, what methods are available for protection against the dangers of sulfur pollution. Setting aside local treatment of pollution at the actual emission source (filtering, conversion, etc), it is first necessary to try to predict the dangers of this type of pollution. For example, attempts will be made to predict the extent of the affected areas. Variations in the pollution must then be observed with the use specialized devices making it possible to detect critical levels.

Simulation methods may be used for prediction. The computer appears to be an obvious choice: on the basis of a mathematical model of the meterological, geographic and geological conditions of the area to be studied, the effects of pollution are simulated, stack heights and smoke plume heights are computed, and the concentration of pollutants on the ground is predicted. Such digital simulation methods are used in the U.S. and in Europe and yield satisfactory results when the parameters are relatively simple: small number of pollutant sources, high stacks, relatively even terrain. On the other hand, with stacks with multiple sources and countryside containing hills, lakes and concentrated urban areas, the process becomes complicated and extremely costly. To alleviate these drawbacks, a group of French researchers from the Center of Experimental Research and Instrumentation of the National Meteorological Commission, directed by Mr. Facy, has developed an original method for visualization of pollution in a hydraulic duct, using the color variations of an emulsion layer containing colored pH indicators, protected by a semipermeable membrane, on the model of the site being studied. This analog method is generally less costly and faster than digital simulation techniques on a computer or simulation on a model in an air duct. This is due to the fact that with air ducts, measurements of concentration for each

wind direction and speed imply long and complex manipulations and an extremely large number of point measurements, requiring use of the air duct on a single model for several months.

Fig. 2. The Securipol Company has developed a new simulation technique designed to measure and predict air pollution (outlined below). This technique makes it possible to trace the development of areas with a high percentage of pollution (red and yellow).

The hydraulic duct procedure is so promising that a new company, Securipol, financed by the EED and Sefinnova, has recently been set up to offer polluting industries, municipalities and government agencies the service of predicting pollutant concentration on the ground as a function of various meteorological conditions and relief. The ANVAR [Agence nationale pour la valorisation de la recherche; National Agency for Valorization of Research] has taken responsibility for the patents on the process, especially those covering the semipermeable layer containing the dyes.

Using the Securipol procedure a simulation may be obtained, first, by constructing a polyvinyl model representing the topography of the site to be studied on a reduction scale which may be as high as 1/10,000. The habitat, forests, prairies, hills and industrial areas are faithfully reproduced on the basis of geographic and geological data. This model, covered with a special indicator layer, is then placed in a test chamber equipped with lateral glass walls. This chamber is traversed by a current of water whose flow rate and turbulence are carefully controlled after it passes through honeycombed diffusion batteries. The ejection stacks, also built to scale, and fixed in their proper positions, emit an acid solution into the water current (which simulates the force and direction of the wind). The emulsion layer placed on the model will change color upon contact with these effluents, thus indicating the ground concentration. At the end of the simulation, one thus obtains an overall visualization of the integrated value of isoconcentrations, varying from red (high concentrations) to green and blue (low concentrations) at different points on the site. Photographs taken during the test make it possible to superimpose the coloration obtained on detailed maps of the region. This highly original method, which is far in advance of techniques currently used in the U.S. and Japan, offers considerable interest in the choice of sites for thermal plants and refineries or in selecting critical points necessitating the installation of detectors for continuous monitoring of pollution levels. Well-placed detectors will gradually make it possible to obtain an ideal system, completely self-regulated, and, in cases when critical levels have been surpassed, one which will automatically trigger either a slowdown in the activity of the thermal plants or replacement of the fuel used by a fuel with low sulfur content.

A Pilot Project in Holland

A system close to the ideal closed loop network has been in operation for the past year near the port of Rotterdam in Holland. The region under observation, the Rijnmond, located between the docks of the port and the North Sea, includes a number of industries, among them refineries and petrochemical plants. Since the pollution in this area had reached danger levels, the Netherlands Institute of Health, Eindhoven Technical University and local industries have developed and installed an observation network consisting of 31 "breathers" connected by telephone lines to a Philips P 9201 computer placed in the control center in Schiedam. Each measuring station includes an automatic SO_2 analyzer and a detector located atop a pole. The position and number of poles were determined by means of a mathematical model: there are always eight stations downwind from pollution sources, no matter what the direction of the wind and the meteorological conditions. Each station measures the SO_2 content in the air and other meteorological parameters, notably the speed and direction of the wind, 64 times every hour. All these data are transmitted to the central computer, which computes the average SO_2 concentration and indicates trends. When critical levels have been exceeded, an automatic warning device alerts the industries in the area so that they can reduce the quantity of their emissions. This system will be extended to all of Holland in 1973. The network will include 250 stations and will cost more than 10 million florins. In view of the success of the initial tests, several Swiss pharmaceutical companies -- Ciba-Geigy, Hoffman-Laroche and Sandoz -- have ordered a system of ten stations for the Frickdal valley close to Bâle. This network will be in operation at the end of this year.

Prevention, detection, treatment, observation -- pollution is increasingly taking on the appearance of a societal disease, with attempts being made

to apply new types of preventive methods. Thanks to monitoring networks and computers, it may be expected that in the fairly near future, industries and thermal plants will be capable of adjusting their emissions to the pollutant content of the atmosphere. Assuming that the same will be true for water, we will be close to obtaining the basic principles for regulating broad natural cycles, cycles which have existed in the ecosystem for aeons but which we have now begun to disturb, endangering the entire biosphere.